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SILICON CARBIDE FIBER/MULLITE COMPOSITES FROM RAPIDLY  
SOLIDIFIED ALUMINOS. (U) PENNSYLVANIA STATE UNIV  
UNIVERSITY PARK DEPT OF MATERIALS SCI.

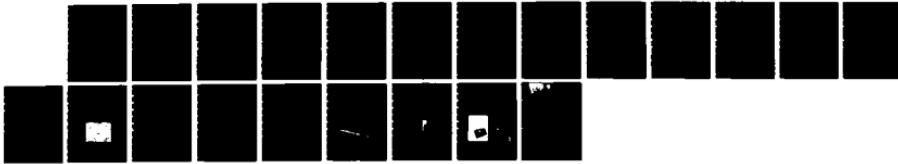
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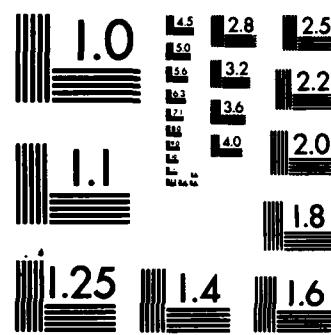
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REPORT DOCUMENTATION PAGE			READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER DAAG29-83-K-0105	2. GOVT ACCESSION NO. 20955		3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Silicon Carbide Fiber/Mullite Composites from Rapidly Solidified Aluminosilicate Powder.		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 6/21/83 - 12/21/83	
6. AUTHOR(s) R. E. Tressler and G. L. Messing		7. CONTRACT OR GRANT NUMBER(s) DAAG29-83-K-0105	
8. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Materials Science and Engineering The Pennsylvania State University University Park, PA 16802		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
10. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		11. REPORT DATE April 1, 1984	
		12. NUMBER OF PAGES 16	
13. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		14. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silicon carbide, fibers, composite, mullite, transient liquid			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) It has been demonstrated that mullite matrix ceramics can be formed by crystallizing an amorphous aluminosilicate powder in the presence of a transient liquid ( $B_2O_3$ ) by hot pressing at 1050°C. A fiber-reinforced composite was fabricated by laying continuous SiC fibers between tape cast layers of the mullite composition and hot pressing at 1050°C and 21 MPa for $\frac{1}{2}$ hr. The mechanical strength and toughness of samples tested perpendicular to the fiber direction were 110 MPa and 1.44 MPa.m <sup>1/2</sup> , respectively. As these results were obtained with a porous, large grain size microstructure, that is not optimized, it is suggested that significant			

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enhancement can be obtained through improvements in microstructure uniformity and density, fiber distribution and by full crystallization of the mullite matrix. Thus, although a feasible method for fabricating SiC fiber reinforced mullite matrix ceramics has been demonstrated, realization of their full potential requires further study.

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**Final Technical Report**

**R. E. Tressler and G. L. Messing**

**April 1, 1984**

**U. S. Army Research Office  
Contract No. DAAG29-83-K-0105**

**Department of Materials Science and Engineering  
The Pennsylvania State University  
University Park, PA 16802**



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## Silicon Carbide Fiber/Mullite Matrix Composites from Rapidly Solidified Aluminosilicate Powder

### Introduction

This study was initiated to test the feasibility of using a rapidly solidified, amorphous powder, which rapidly crystallizes to mullite as it is thermal cycled to ~980°C, to fabricate ceramic matrix composites using SiC fibers. The novel idea is the use of transient liquid additives to accelerate the densification of the amorphous powders and the conversion of the matrix to the crystalline oxides either during the fabrication process or by a subsequent heat treatment.

The specific rapidly solidified material chosen was the ~60 weight %  $\text{Al}_2\text{O}_3$ , ~40 weight %  $\text{SiO}_2$  Fiberfrax H insulating fibers fabricated by the Carborundum Company. By milling, these fibers were reduced to processible powders. Boric oxide in the form of boric acid and anhydrous  $\text{B}_2\text{O}_3$  was used as the transient liquid phase additive because it can be incorporated into the mullite structure due to the complete mullite solid solution between the  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and  $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$  end members. A secondary cristobalite phase is known to crystallize at higher temperatures (1200–1300°C), thus consuming the high silica glass that is rejected during the crystallization of the mullite (~73%  $\text{Al}_2\text{O}_3$ ).

The fibers which were readily available for this study were the Nicalon® amorphous or microcrystalline SiC fibers which have high Si and C contents but also contain a few percent of oxygen.

The study was designed to test the feasibility of fabricating composites of high density using these materials and to characterize the properties of these composites. We also performed studies on the strength of the fibers as affected by heat treatment.

### Experimental

#### Sample Preparation

Amorphous aluminosilicate powder was obtained by dry ball milling Carborundum's high temperature insulation known as Fiberfrax H. This is a fibrous material that is produced in commercial quantities by supersonic airblast quenching a melt of ~60%  $\text{Al}_2\text{O}_3$  and ~40%  $\text{SiO}_2$ . A powder with a nominal particle size of 10 microns was obtained by dry ball milling the fibrous insulation for 18 hours in an alumina mill with 1/4 inch cylindrical media.

In initial experiments, boron oxide was added by dissolving boric acid in water and then adding enough aluminosilicate (AS) powder to the solution to yield a net composition of 10%  $\text{B}_2\text{O}_3$  and 90% AS. An acrylic emulsion binder was added to the slurry. The slurry was hand granulated by drying and size classified by passing the granulated powder through a 40 mesh screen. Samples of 2.5 cm diameter by 1.2 cm height were uniaxially pressed at 207 MPa.

An alternative process for adding  $\text{B}_2\text{O}_3$  was developed because of heterogeneity problems associated with the use of boric acid. This method involved adding solid anhydrous  $\text{B}_2\text{O}_3$  to a slurry of AS in tolene. This mixture was mixed and milled in a polyethylene jar with 1/4 inch alumina media. After milling for 8 h, 3 weight % polyvinyl butyral binder (Cladan) was added and the mixture milled an additional 2 h. For dry pressing, the mixture was dried and granulated to ~40 mesh. For laminated composite structures the slurry was cast onto a coated glass plate with a hand held doctor blade to produce 0.5 mm thick AS tape.

Composite structures of SiC fibers and a matrix of AS plus  $\text{B}_2\text{O}_3$  were fabricated after experiments with the AS plus  $\text{B}_2\text{O}_3$ . The composite samples were fabricated by laying SiC fibers between AS plus  $\text{B}_2\text{O}_3$  tape. Before SiC fibers were used, the resin sizing that was

applied to them after their synthesis was removed by heating at 500°C for 1/2 h in air. The fibers were laid across a 2.5 cm square of the AS plus B<sub>2</sub>O<sub>3</sub> tape and held in place by coating the fiber/tape surface with the tape slurry. After drying, the excess fibers were cut to yield a 2.5 cm square tape with unidirectionally oriented SiC fibers. A composite monolith was formed by stacking 25 of these layers, such that the SiC fibers were aligned, and then pressing the multilayer at 70°C and 21 MPa. Before hot pressing the organics were removed by heating the composite at 1°C/min to 250°C and then 0.5°C/min to 300°C and then holding at 250°C for 18 h.

Both pressed samples of the matrix composition and composites were hot pressed in standard graphite tooling. Samples were heated at 5°C/min to 1050°C and held for 1/2 h. A pressure of 21 MPa was applied when the sample reached 850°C. Table 1 summarizes the samples that were fabricated and hot pressed.

#### Mechanical Property Determinations

Strength tests on individual fibers were made by first burning off the polyvinyl acetate fiber coating and then dispersing the fibers in an organic liquid so that individual fibers of 7.5 cm in length could be selected.

The tests were performed by bonding the fibers to a thin index card paper specimen support which was perforated with a 1.2 cm diameter hole in the mid-section. A structural epoxy was chosen as the adhesive for bonding the fiber to the paper all along its length except for the central 1.2 cm. This central region represents the eventual gauge length in the tensile test. The ends of the cardboard specimen holder, outboard of the fiber ends, were gripped in pneumatically operated grips on universal joints in a table model Instron and tested at a strain rate of 0.1 cm/cm/min. Before the test, the fiber diameter

in the gauge length was carefully measured with a calibrated fiber eyepiece in an optical microscope.

Individual fibers were heat treated in air and in argon by supporting the fibers near their ends on SiC supports at temperatures of 600, 800, 1000, 1200 and 1400°C. These fibers were then tested as described above. SEM and optical micrographs were taken of fracture surfaces of many of the fibers from the extremes of the strength distributions.

A limited number of strength specimens and single edge-notched beam specimens were cut from billets of the 15% B<sub>2</sub>O<sub>3</sub> and 25% B<sub>2</sub>O<sub>3</sub> compositions. These specimens were all approximately 0.3 cm x 0.3 cm x 3 cm in size. The notched beam tests were run at a crosshead speed of 0.25 cm/min as were the strength specimens. All of these tests were run in four point bend and the samples were carefully dried at 200°C for several hours before testing to eliminate any absorbed H<sub>2</sub>O in the pores in the materials.

These tests were performed with the crack running perpendicular to the unidirectionally oriented fibers which should yield the maximum in toughness and strength.

#### X-Ray Diffraction

XRD scans were performed on the hot-pressed matrix mixtures and on the hot-pressed composites fabricated under identical conditions. The patterns were compared to those in the JCPD file to determine the identities of the crystalline phases present after the hot-pressing cycles.

#### Results

#### Densification

A series of experiments on the matrix composition were carried out to establish appropriate processing parameters. In the initial experiments, boric acid was the precursor for B<sub>2</sub>O<sub>3</sub>. Samples 1 and 2 had 10 weight %

$B_2O_3$  and a green density of  $2.02 \text{ g/cm}^3$ . Samples 1 and 2 were hot pressed by applying pressure at room temperature and  $850^\circ\text{C}$ , respectively. The hot pressed densities were  $2.39$  and  $2.36 \text{ g/cm}^3$  and the shrinkages were 26 and 20 volume % for samples 1 and 2, respectively. This data suggests that the time at which pressure is applied to the matrix composition is unimportant for densification. Therefore, all other samples were hot pressed by applying pressure at  $850^\circ\text{C}$ . The microstructures were characterized by large ( $>0.1\text{mm}$ ) voids in an otherwise dense microstructure. The voids are attributed to the formation of large boric acid precipitates that were formed during powder preparation. On heating, the boric acid melts and is redistributed by capillarity into the matrix powder structure leaving a large void. To prevent void formation by this mechanism, anhydrous  $B_2O_3$  was used instead of the boric acid.

Matrix samples with 10-25 weight% anhydrous  $B_2O_3$  were dry pressed and hot pressed. The hot pressed densities ranged from  $2.39$  to  $2.47 \text{ g/cm}^3$  and from microscopy, the porosity was estimated to be 15-20 %. In these samples, there was no evidence of the gross porosity that was noted above (Figure 1). The densities indicate that densification is not affected by the amount of liquid for these experimental conditions. It is important to note that densification occurred as soon as pressure was applied and continued until  $1050^\circ\text{C}$ . The densification at  $T < 980^\circ\text{C}$  is attributed to the rearrangement of the microstructure in the presence of the  $B_2O_3$  liquid ( $T_m=470^\circ\text{C}$ ). At  $980^\circ\text{C}$  the AS powder crystallizes to mullite and a distinct increase in the densification kinetics is observed as monitored by the displacement of the hot pressing ram. Unfortunately, there is insufficient data at this time to quantify the relative importance of these two densification mechanisms or to quantify their fundamental contributions.

Two multilayer composites were fabricated with hot-pressed dimensions of 5 cm diameter and ~7 mm thickness. These samples differed in  $B_2O_3$  content and fiber content. The composite with 15%  $B_2O_3$  was fabricated first and was characterized by a density of  $2.55\text{ g/cm}^3$ . The preliminary mechanical testing on samples machined from this composite suggested that there was insufficient bonding of the SiC fibers in the mullite matrix. Therefore, a composite with 25%  $B_2O_3$  and fewer fibers between the layers was fabricated. It was thought that the additional liquid provided by the increased  $B_2O_3$  content would enhance laminate bonding during hot pressing. The composite was characterized by a density of  $2.3\text{ g/cm}^3$  and a more uniform structure. The difference in density is attributed to the presence of fewer SiC fibers between the layers.

#### X-Ray Diffraction

In all of the hot pressed specimens fabricated at the maximum temperature of  $1050^\circ C$ , mullite was the primary matrix phase and also contained some glassy phase as evidenced by the "amorphous hump" in the XRD patterns. There was also a trace of crystalline  $B_2O_3$  which must be located in isolated pockets which incompletely reacted with the  $Al_2O_3$  and  $SiO_2$ . These pockets of  $B_2O_3$  ( $T_m=410^\circ C$ ) probably melted and recrystallized upon cooling. In all samples containing 20 and 25%  $B_2O_3$  the  $9Al_2O_3 \cdot 2B_2O_3$  phase was detected in small amounts by XRD. Cristobalite was not detected since the samples were not heated above  $1050^\circ C$ . Clearly, a careful study of higher temperature heat treatment effects on continued reactivity and crystallization is very important to fully assess the potential of this composite fabrication approach.

### Mechanical Properties

In Figures 2 and 3, the effects of heat treatment for 24 hours in argon and air on the strength distributions of the fibers are presented. We see the surprising result that even at a temperature as low as 600°C that the fibers are severely degraded by heat treatment. In Figure 4, the average strengths as a function of temperature are presented. The fact that the 1400°C treatment in air does not as seriously degrade the strength as the lower temperature treatments is somewhat surprising, but in examining the fibers carefully (Figure 5) we find that the fiber is sheathed in glass which tends to form beads periodically along the length, presumably due to surface tension forces. Therefore, the surface of the fiber is quite defect free due to this, apparently, thermally grown oxide glass layer.

On the fracture surfaces we see evidence of surface fracture origins in the weaker fibers and internal origins in the stronger fibers which have the oxide sheath.

These rather low strengths after moderate heat treatments, raise serious questions about the efficiency of this fiber as a reinforcement in the intermediate temperature range.

Our preliminary mechanical property measurements on the notably less than optimized composites are somewhat encouraging. For the 25% B<sub>2</sub>O<sub>3</sub> composites, we measured K<sub>IC</sub> values averaging 1.44 MPa.m<sup>1/2</sup> which is more than double what one expects for a silicate glass. The mode of crack propagation (Figure 6) is most encouraging. We see fibers bridging the crack opening and deflection of the crack tip at its intersection with fibers. The crack propagation is, however, quite planar, unlike the fracture mode in the toughest glass-ceramics such as the UTRC Compglas. Thus, considerably more work is in needed to optimize the distribution of fibers, interface bonding, and

densification in order to optimize the toughness. Clearly, the crystallization of the cristobalite and elimination of the glass will improve the mechanical properties.

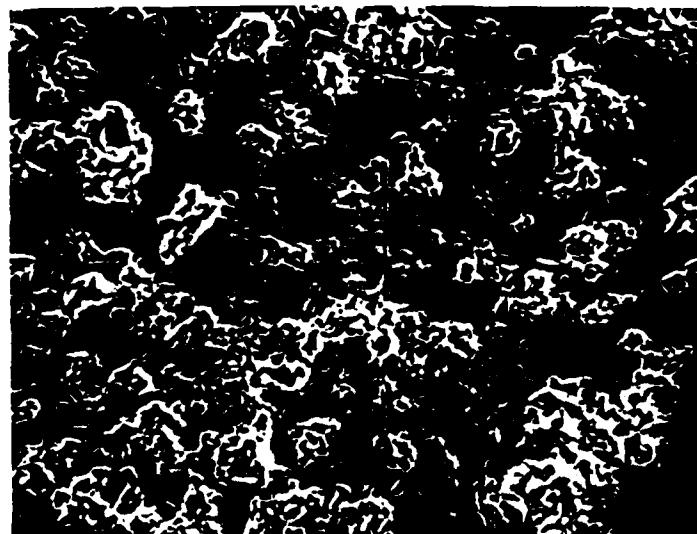
The corresponding strengths of this 25%  $B_2O_3$  materials averaged 110 MPa. We were not able to retain a plate of sufficient dimensions to make elastic modulus measurements. The fracture surfaces (Figure 7) show evidence of extensive fiber pullout and crack deflection.

For the 15%  $B_2O_3$  composite, the single edge notched beams never really completely fractured but rather, delaminated and debonded along the lengths of the fibers, thus absorbing much energy. The  $K_{IC}$  values calculated from these tests have little meaning since the cracks were far from planar. But qualitatively, the toughness and energy absorption was much greater than for the 25%  $B_2O_3$  composite.

Table 1. Compositions, Shrinkage and Density of Hot Pressed Samples

Sample No.	Composition (w/o)	Shrinkage (v/o)	Density (g/cm <sup>3</sup> )
1	90% AS + 10% B <sub>2</sub> O <sub>3</sub> (H <sub>3</sub> BO <sub>3</sub> as source)	26	2.39
2	90% AS + 10% B <sub>2</sub> O <sub>3</sub>	25	2.36
3	85% AS + 15% B <sub>2</sub> O <sub>3</sub>	27	2.47
4	80% AS + 20% B <sub>2</sub> O <sub>3</sub>	20	-
5	75% AS + 25% B <sub>2</sub> O <sub>3</sub>	24	2.47
6	85% AS + 15% B <sub>2</sub> O <sub>3</sub> + Fibers	50	2.55
7	75% AS + 25% B <sub>2</sub> O <sub>3</sub> + Fibers	43	2.3

AS = aluminosilicate powder



**Figure 1.** SEM micrograph of a typical microstructure of the mullite matrix (Sample 2). 500X

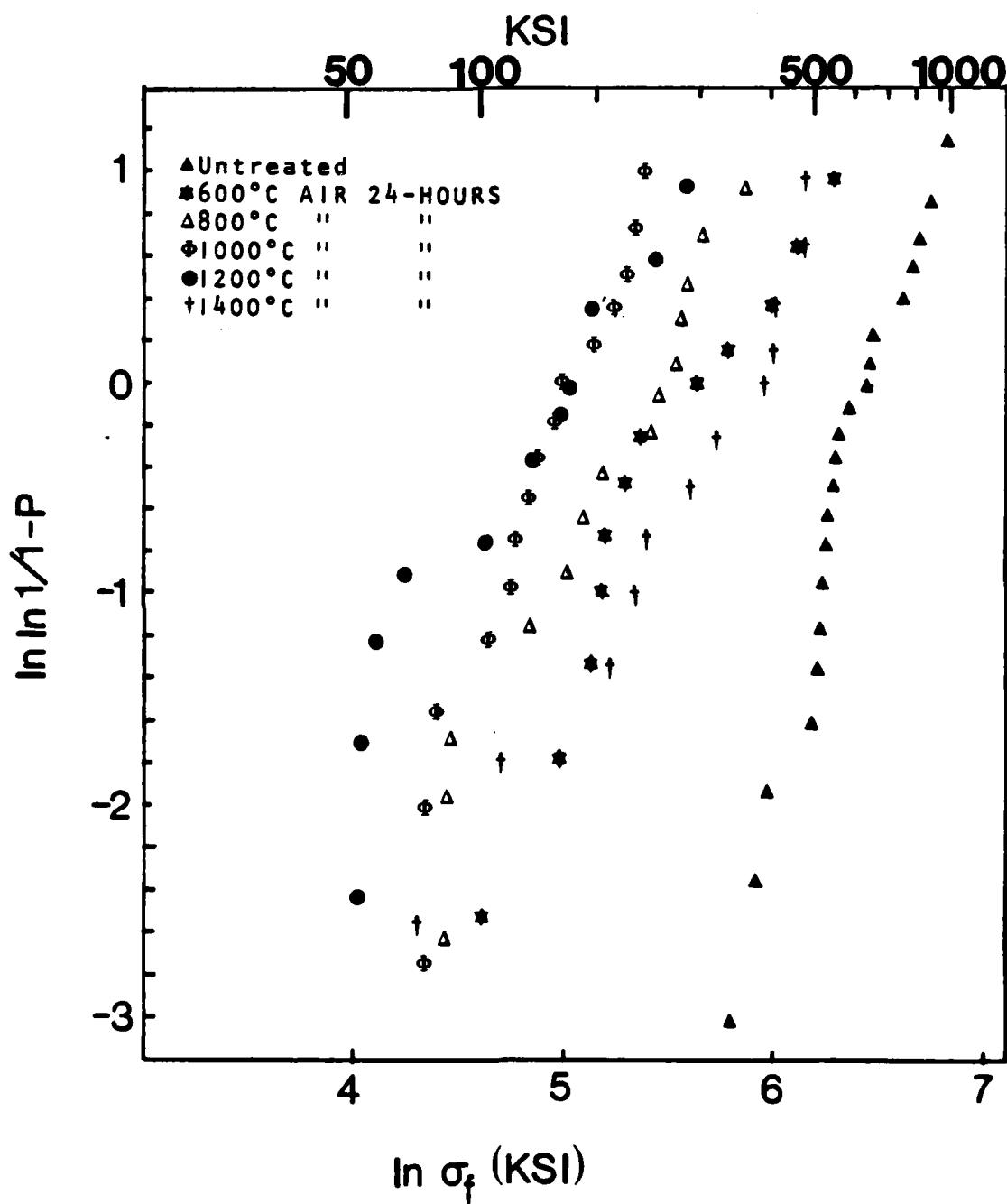


Figure 2. Strength distributions of Nicalon fibers as received and after heat treatment in air for 24 hours.

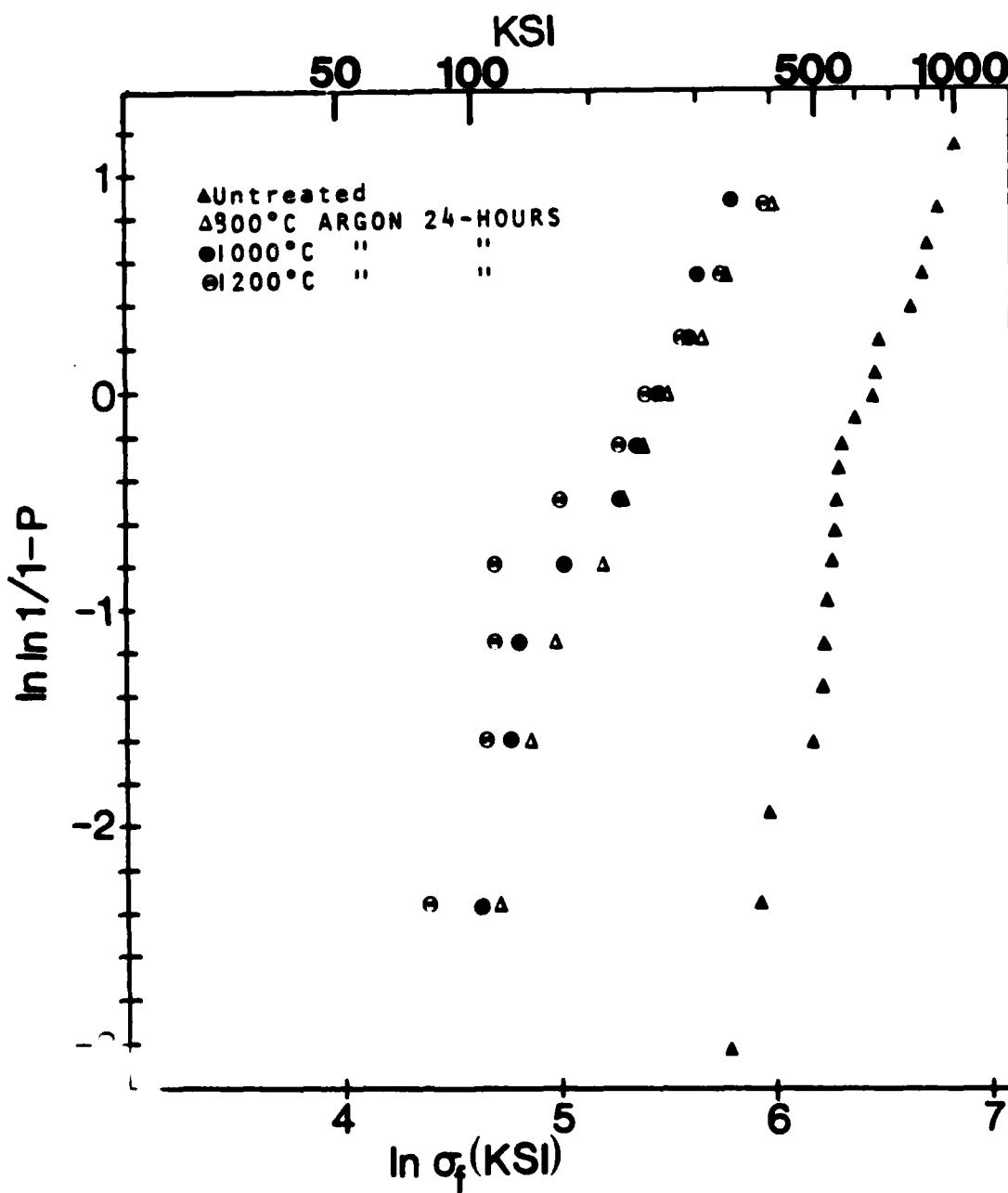


Figure 3. Strength distributions of Nicalon fibers as received and after heat treatment in argon for 24 hours.

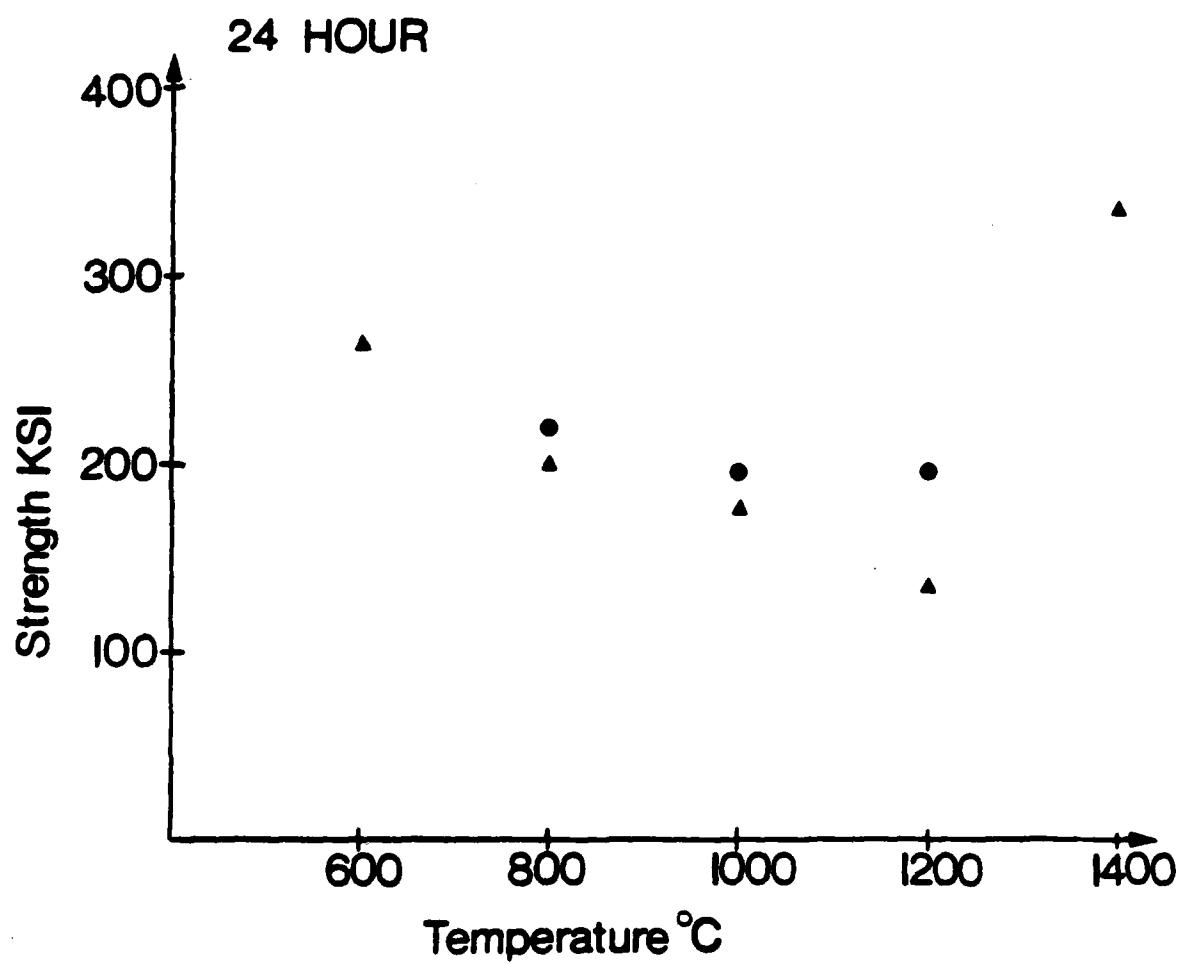


Figure 4. Average strengths of Nicalon fibers versus heat treatment temperature. ▲ Argon ● Air

**24 HR AIR  
1400C**



**Figure 5.** Optical micrograph of a Nicalon fiber after heat treatment for 24 hours in air.



Figure 6. Arrested crack in a SENB specimen showing fibers bridging the crack opening and deflection of the crack by fiber layers.

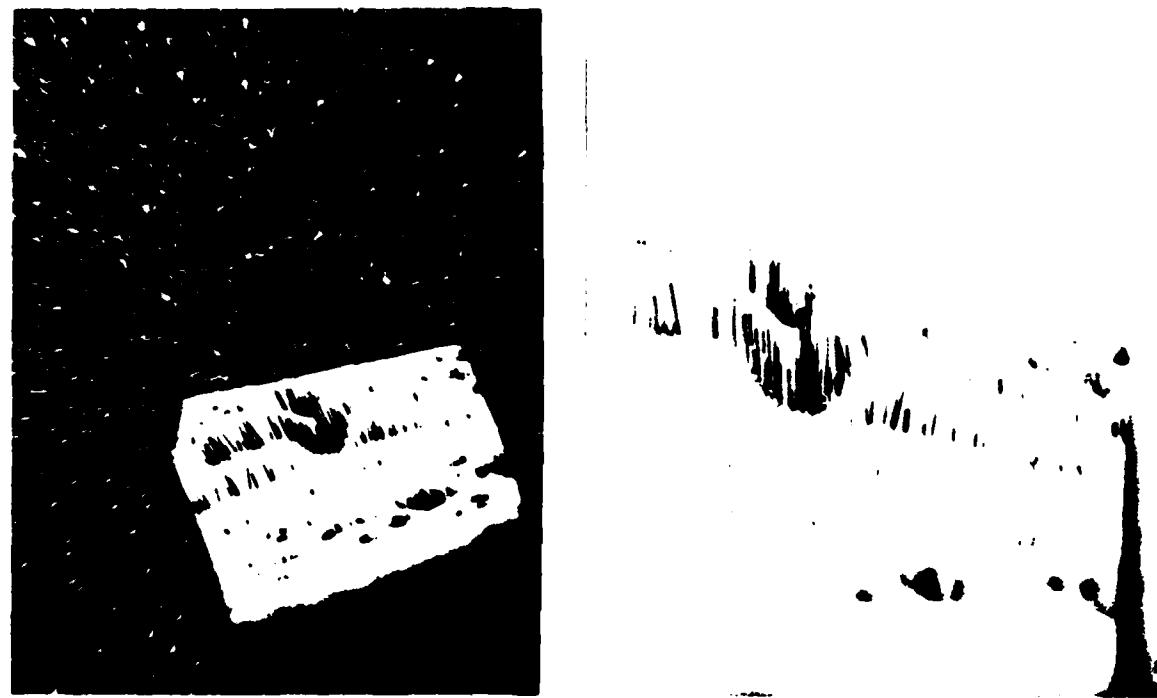


Figure 7. Optical micrographs of the fracture surface of a 25%  $B_2O_3$  composite specimen.

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